Comparison of Toluene Distillation and Karl Fischer Methods for Determining Moisture in Dry Whole Milk

2784

EDWARD S. DELLA MONICA and T. F. HOLDEN [1]

Eastern Utilization Research and Development Division, USDA
Philadelphia, Pennsylvania

Abstract

The toluene distillation and Karl Fischer methods for determining the moisture content of dried whole milk were compared. In this study both methods were employed simultaneously with a single sample. The study also included noncomparative data, i.e., analytical data obtained by one or the other method. The data were compared at four moisture ranges. In the comparative study the statistical analysis was between methods and operators. The statistical analysis of the noncomparative data was between moisture levels, for each operator and method. The results of the first comparison indicate that the mean value by the Karl Fischer method was almost identical to that obtained by toluene distillation. The statistical evaluation illustrated that the two methods do not have the same precision, especially above 7% moisture. From 0 to 7% moisture the toluene method is more precise, having confidence limits (for duplicates) of ±0.130 to 0.199. The confidence limits for Karl Fischer titration ranged from ±0.130 to 0.292. The results also indicate the existence of operator differences with both methods.

In the development of the vacuum foam drying process for producing whole milk powder, a rapid and accurate method for determining the moisture content of the product is essential. The Dry Milk Institute (2) lists toluene distillation as its official method. This method, however, has certain disadvantages, e.g., the toluene is flammable, large samples (50 to 100 g) are required, and special glassware is needed. The Dry Milk Institute also lists the Karl Fischer titration as a tentative method for determining moisture in milk powders. Heinemann (4) compared these two methods for determining moisture and concluded that the Karl Fischer titration was satisfactory, provided the samples contained less than 20% moisture. He also indicated that the direct titration technique gave satisfactory results. Heinemann, however, has only indicated the numerical difference between values obtained by each method. For this reason it was thought advisable to study the Karl Fischer method more extensively.

All the data were obtained by determining the moisture content of numerous experimental whole milk powders produced throughout a two-year period. The comparative and noncomparative studies were conducted during the investigation period. In the comparative study the toluene distillation and Karl Fischer titration methods were employed simultaneously for determining the moisture content of a single powder. In the noncomparative study each sample was analyzed by one or the other method.

Preliminary observations indicated that the moisture level influenced the accuracy of both the Karl Fischer and the toluene determinations. Therefore, the data were divided into four ranges, with these ranges corresponding to the usual moisture content of the milk powder as sampled at four selected regions in the dryer. Four operators carried out the moisture determinations. The data were compared at the four moisture ranges, between methods and between operators.

Experimental Procedure

Apparatus. A Beckman KF-3 Aquameter[2] equipped with duo platinum electrode (39032) was used for all Karl Fischer titrations (5). The burette assembly consisted of a 10-ml pressure-filled automatic zero type burette, with a valve-controlled delivery tip. Magnetic stirrers were used for agitating the samples. The accepted toluene distillation apparatus (2), employing a 5-ml Bidwell-Sterling distilling receiver[2] (3), was used for that determination.

Reagents. Karl Fischer Reagent stabilized, single solution, was the titrant for that determination. Toluene and methanol were reagent grade.

Procedure. Whole milk powders, produced by the process of Aceto et al. (1), were used in this

Received for publication July 10, 1967.

[1] Present address: The Lubrizol Corporation, 23100 Lakeland Boulevard, Wickliffe, Ohio 44092.

[2] Reference to certain products or companies does not imply an endorsement by the Department over others not mentioned.

study. All powders were passed through a 20-mesh screen and placed in sealed jars. The milk powders were analyzed by both methods on the same day to minimize atmospheric moisture contamination. Both toluene and Karl Fischer determinations were done in duplicate.

Toluene distillation. From 20 to 50 g of milk powder, to yield approximately 2 to 4 ml H_2O, were weighed into a 500-ml Erlenmeyer flask having a 24/40 ground glass joint. Approximately 250 ml toluene was added and distillation carried out as described (2). Values are reported as per cent moisture on a wet basis.

Karl Fischer. Exactly 100 ml methanol was added to a 125-ml Erlenmeyer flask containing from 1.0 to 3.0 g of milk powder. Constant agitation for 1 hr with a magnetic stirrer facilitated extraction of water from the milk powder. After allowing the powder to settle, a 10.0-ml aliquot of the methanol extract was withdrawn and placed in a 300-ml titration vessel. During transfer of sample the vessel was continuously purged with dry nitrogen to minimize atmospheric moisture contamination. The amount of KF reagent required to predry the diluting solvent was determined daily. This constituted the blank value for the methanol used and was subtracted from all standard and sample titrations. Also, a water-methanol standard containing 150 to 200 mg of water in a total volume of 100 ml methanol was prepared daily. An aliquot containing approximately 15 to 20 mg H_2O was titrated to determine the Karl Fischer water equivalent. The water equivalent value is expressed as mg H_2O per ml Karl Fischer reagent.

Calculation.

$$\% \text{ Moisture} = \frac{(\text{Sample Titer} - \text{Blank Titer}) \times (\text{Water Equivalent}) \times 100}{\text{Weight of Sample in Mg}}$$

Note: Water equivalent and blank titer were determined daily.

Results and Discussion

Duplicate analyses permitted statistical evaluation of the data by a One-Way Analysis of Variance (ANOVA). For these data, the ANOVA was applied to a particular treatment—i.e., a group of data having in common such factors as a specific method, moisture level, and operator. These computations yield a within treatment variance as well as a between treatment variance. The former is a measure of the repeatability of any set of duplicate analyses within a single treatment. The between treatment variance term, because of the extended range of moistures covered (0 to 10%), was expected and found to be very high and of little value in this study. The within treatment variance terms, however, are of great importance, in that the relative precision of two treatments differing in only one factor can be determined by calculating the F ratio of the two variances.

The data also were evaluated to determine the relative bias between any two common treatments—e.g., the two methods studied. In these computations the grand means of the two treatments being tested were compared by Student's "t" test.

The confidence limits betwen duplicates also were calculated.

An IBM 1130 Computer[2] was employed for all computations.

"t" Test. Presented first are the results of a comparative study of the two analytical methods (Table 1). To minimize the influence of moisture content the data have been stratified according to moisture range, and within each range according to operator and method. All four operators accumulated data in the 0 to 4% moisture range, while only one operator had comparative data in the 7% and over ranges. Three of the four obtained results at the 4 to 7% level. The mean value for each set of data was calculated, then compared statistically, using a "t" test. The comparisons were between methods at each moisture level and for each operator. The results show no significant difference between the mean values, indicating that both methods are equally reliable for determining the moisture content of whole milk powders. This held true for each operator and within each moisture range. The precision of the two methods, however, was found to vary somewhat.

Measure of precision. The precision of two sets of measurements can be compared by calculating the ratio of their variances. Thus, the two within group variances between methods were compared. The comparisons were made for each operator and at each moisture level. Known as the F ratio, this calculation shows (Table 1) that in all but one case (up to 7% moisture) no significant difference in the precision of each method was found. In the single exception, the toluene distillation was the more precise method. Above 7% moisture, significant differences were observed, with the Karl Fischer titration being more precise from 7 to 10% H_2O, and the distillation method giving better results over 10% H_2O. It should be noted, however, that this conclusion is based on the results obtained with only one operator, thus preventing any between operator comparisons at these higher moisture levels.

A noncomparative study—i.e., each sample was analyzed by one or the other method—also

TABLE 1

Comparative data for both methods

Moisture range	Operator	Method of analysis	No. of observations	Grand mean (%)	"t" Test (grand mean)	"F" ratio (within group variance)
0–4%	A	Tol	24	3.86	0.803	2.36*
	A	KF	24	3.80		
	B	Tol	160	3.49	0.032	1.07
	B	KF	160	3.49		
	C	Tol	116	3.40	0.277	1.04
	C	KF	116	3.41		
	D	Tol	50	3.68	1.38	1.32
	D	KF	50	3.78		
4–7%	A	Tol	46	4.66	0.251	1.01
	A	KF	46	4.63		
	B	Tol	82	4.61	0.023	1.07
	B	KF	82	4.61		
	C	Tol	56	5.17	0.061	1.36
	C	KF	56	5.18		
7–10%	C	Tol	30	8.23	0.412	3.34*
	C	KF	30	8.49		
>10%	C	Tol	22	12.75	1.06	10.33**
	C	KF	22	13.48		

* Significant (P = 0.05).
** Highly significant.

was undertaken. These data, Tables 2 and 3, were utilized to determine more precisely the within treatment variance. The F ratio comparing adjacent moisture ranges is presented for each operator. The results illustrate that for each method all but one operator showed no significant difference in precision between the 0 to 4 and 4 to 7% range. Above 7% moisture, significant differences were observed. Inasmuch as not all operators tested samples in all moisture ranges, the statistical analysis was not carried any further. From this it is concluded that stratification of data below the 7% moisture level is unnecessary. Above this level, however,

TABLE 2

Within group variance for each operator, between moisture ranges: The Karl Fischer method

Operator	Moisture range (%)	Degrees of freedom[a]	Confidence limits for duplicates P = 0.05	Within group mean squares $\times 10^{-2}$	"F" ratio
A	0–4	28	±0.220	2.305	1.24
	4–7	46	0.194	1.862	6.06*
	7–10	11	0.521	11.275	1.02
	>10	23	0.497	11.525	
B	0–4	80	0.149	1.124	1.28
	4–7	41	0.178	1.553	1.38
	7–10	30	0.235	2.640	2.32*
	>10	124	0.346	6.120	
C	0–4	58	0.133	0.883	1.56
	4–7	28	0.170	1.381	1.08
	7–10	15	0.184	1.496	26.56**
	>10	11	0.979	39.722	
D	0–4	68	0.167	1.403	2.99*
	4–7	44	0.292	4.199	2.31*
	7–10	18	0.463	9.693	1.27
	>10	42	0.500	12.262	

[a] Degrees of freedom = number of observations ÷ 2.
* Significant (P = 0.05).
** Highly significant (P = 0.05).

TABLE 3

Within group variance for each operator, between moisture ranges: Toluene distillation method

Operator	Moisture range (%)	Degrees of freedom[a]	Confidence limits for duplicates P = 0.05	Within group mean squares $\times 10^{-2}$	"F" ratio
A	0–4	12	±0.192	1.560	1.73
	4–7	23	0.139	0.902	
B	0–4	80	0.154	1.205	1.19
	4–7	41	0.171	1.436	
C	0–4	58	0.130	0.847	2.22*
	4–7	28	0.199	1.880	2.65*
	7–10	15	0.337	4.990	1.30
	>10	11	0.305	3.845	

[a] Degrees of freedom = number of observations ÷ 2.
* Significant.

the precision of duplicate determinations becomes somewhat poorer, thereby necessitating stratification to minimize the effect of the moisture content on the confidence limits of duplicates.

Confidence limits. By utilizing the within group variance (mean square value) and the appropriate "t" value, the confidence limits for any number of replicates may be calculated. Duplicate analyses were run in this study; consequently, the confidence limits for duplicates were determined. These data (Tables 2 and 3) show the effect of moisture level on the confidence limits. With the toluene method (0 to 7% moisture) the confidence limits are confined to a relatively narrow range (±0.130 to 0.199.). The Karl Fischer titration shows somewhat greater limits (±0.130 to 0.292). Although this suggests that the toluene method has somewhat less difference between duplicates, the other statistical comparisons indicate that the methods are equally reliable for estimating the moisture content of whole milk powders. Above the 7% moisture level, a significant difference in the confidence limits was found for each operator. The Karl Fischer method appears to be the more inaccurate of the two in the higher moisture ranges. However, this may be due to lack of sufficient data for the toluene method in the higher moisture ranges.

The within group mean square values were also used to compare operator differences for each moisture range and method. The results indicate the existence of operator differences with both methods.

In conclusion, it can be seen that moisture values determined by Karl Fischer titration essentially duplicated the results obtained with the toluene distillation. Both methods are comparable in precision in the 0 to 7% moisture range. Above 7%, differences are found for both methods, with the Karl Fischer method appearing to be less precise.

Acknowledgment

The authors are indebted to William Colver, Linda Manerchia, Maurice Snook, Theodore Erdman, and Ronald Korsin for performing the numerous moisture analyses. We also thank James C. Craig, Jr. for his helpful comments concerning the statistical calculations.

References

(1) Aceto, N. C., Sinnamon, H. I., Schoppet, E. F., and Eskew, R. K. 1962. Continuous Vacuum Drying of Whole Milk Foam. J. Dairy Sci., 45: 501.

(2) American Dry Milk Inst. 1955. Bull. 913 (Rev.).

(3) Bidwell, G. L., and Sterling, W. F. 1925. Preliminary Notes on the Direct Determination of Moisture. J. Ass. Off. Agr. Chemists, 8: 295.

(4) Heinemann, B. 1945. Volumetric Determination of Moisture in Dairy Products. J. Dairy Sci., 28: 845.

(5) Mitchell, J., Jr., and Smith, D. M. 1948. Aquametry. Interscience Publ. Inc., New York.